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FINAL REPORT

An Analytical Approach to the Selection of the Reaction Coordinate
in the Calculation of Reaction Profiles

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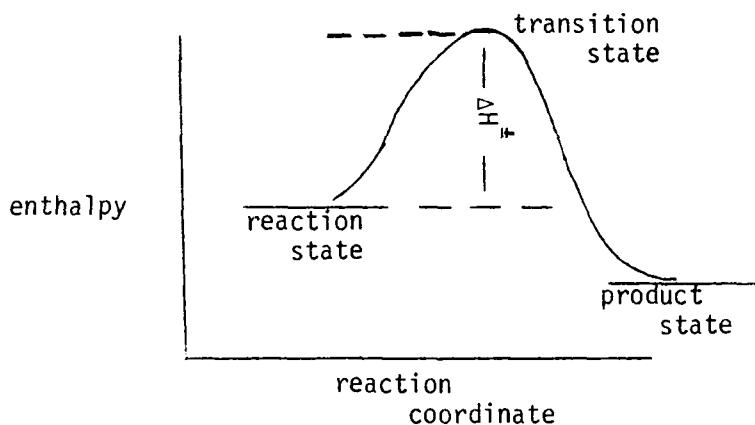
ABSTRACT

An algebraic method for the analytical determination of an expression for the reaction coordinate in an arbitrary potential energy surface is presented. The method is applied to the thionyl imide - thiazyl S hydrozide isomerization reaction. The extent to which the method leads only to required reaction coordinate is dependent upon the manner in which the potential energy surface is sampled to obtain input data for the calculations.

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INTRODUCTION

Present semi empirical molecular orbital methods based upon the modified Neglect of Differential Overlap, i.e. MNDO and MNDO/3, enable the geometry of a molecule in its electronic ground state to be accurately calculated.⁽¹⁾ The method also provides a reasonable accurate estimate of the standard enthalpy of formation.⁽²⁾ As such the MNDO method can be utilized for the calculation of the enthalpy of activation along a reaction path and thus provides thermodynamic information about a reaction mechanism. This is generally accomplished by the selection of a "reaction coordinate" and performing a series of calculations for various values of this "reaction coordinate" being certain that the calculation connects the appropriate reactant and product states. This is shown symbolically in the figure below:⁽³⁾



The state of maximum energy or "transition state" is identified by its maximum energy at a particular value of the reaction coordinate. If the calculations have been properly carried out, a normal coordinate analysis of this transition state (using harmonic oscillator potential functions) produces one negative vibrational frequency for the oscillator which corresponds to vibrational motion along the reaction coordinate.⁽⁴⁾

In principle the method is straight forward, but in practice certain difficulties arise:

1. One generally has no a priori knowledge of the geometry of the transition state and must thus make no assumption concerning its geometrical structure. Each assumption about geometry limits the class of reaction path to be examined.
2. One frequently encounters energy maxima which are not true transition states. (5)
3. A large number of variables have to be examined in a systematic manner. This generally implies that a large number of calculations must be carried out. The procedure can be systemized somewhat by the use of "grid searches,"⁽⁶⁾ but the number of calculations required is still far in excess of what would be required if one had direct knowledge of the reaction coordinate.

The principal difficulty in this type of calculation is the recognition of what to use for the reaction coordinate. The energy calculations are performed in terms of a set of cartesian type coordinates, which are determined from a set of internal coordinates in turn composed of the bond lengths, the bond angles and the dihedral angles necessary to specify the geometry of the molecule(s). Since the geometry of the transition state is not known a priori, the transformation which relates the reaction coordinate to the internal coordinates is not known.

Furthermore experience has shown that the reaction coordinate does not correspond to a single internal coordinate or a linear combination of two or three internal coordinates but is rather more complicated.⁽⁷⁾ At the present time reaction coordinates are identified by a "trial and error" procedure, wherein calculations are performed by variation of one or more coordinates in the internal basis set until the transition state is found. The procedure is very inefficient because of the existence of other maximum on the multi-dimensional energy surface, and the trial and error method in fact becomes intractable for systems which require a large number of coordinates. The

development of a method which would lead to a systematic identification of the reaction coordinate would considerably enhance our ability to perform calculations of reaction profiles.

METHOD

As pointed out in the introduction, one of the principal difficulties encountered in the calculation of the profile of a chemical reaction is the recognition of what to use for the reaction coordinate on a given reaction mechanism. The reaction coordinate is generally not a simple atom-atom distance, bond angle or dihedral angle but it is expressible as a linear combination of these atom-atom distances, bond angles and dihedral angles. Furthermore, it can be expected to contain those coordinates which change markedly as one proceeds from the reactant state to product state. The actual reaction coordinate can be identified and an analytical expression obtained for it by the method outlined below.

A comparison of the geometrical structures of the reactant and product molecules enables one to identify which internal coordinate undergoes a marked change as one passes from the reactant state to the product state. The reactant and product molecules must of course be defined using the same set of internal coordinates (i.e. bond distances, bond angles and dihedral angles). This can always be done. Let the subset of internal coordinates so identified be denoted by $|q_i|$. Suppose n such coordinates are required. The reaction coordinate, ϕ , can be expressed as a linear combination of the $|q_i|$, i.e.

$$\phi = \sum_i^n \alpha_i q_i \quad (1)$$

Explicit determination of the reaction coordinate requires a knowledge of the coefficients $|\alpha_i|$. To a good approximation the energy of the system is a parabolic function of the reaction coordinate and we can write

$$E(\phi) = A\phi^2 + B\phi + C \quad (2)$$

This is certainly true in the vicinity of the transition state and probably valid in regions not too far removed from the transition state. Since we

are always seeking a transition state, E is a maximum for such a state and the calculus tells us that $A < 0$ and $B > 0$.

An arbitrary selection of k sets of values for the $|q_i|$ enables one to calculate k values of the energy, E . If we assume the energy is a quadratic function of the internal coordinates, $|q|$, we can write

$$E = \sum_i \sum_j a_{ij} q_i q_j + \sum_j b_j q_j + c \quad (3)$$

Let q_{1m} denote the value of the internal coordinate q_1 in the set m . The above calculations enable us to write down a set of $n \times (n+3)/2$ equations which can be viewed as a set of linear algebraic simultaneous equations in the coefficients $|a_{ij}|$, $|b_j|$ and c . Namely,

$$E_k = \sum_i \sum_j a_{ij} q_{ik} q_{jk} + \sum_j b_j q_{jk} + c \quad (4)$$

$$k = 1, 2, 3 \dots n(n+3)/2$$

These equations can be solved to obtain values of the coefficients $|a_{ij}|$, $|b_j|$ and c . These coefficients are in turn related to the coefficients of equation (1), $|\alpha_i|$. Namely using equations (1), (2) and (4) from the quadratic term we obtain:

$$a_{ij} = A \alpha_i \alpha_j \quad (i, j = 1, 2 \dots n) \quad (5)$$

from the linear terms we get:

$$b_i = B \alpha_i \quad (i = 1, 2, 3 \dots n) \quad (6)$$

and finally;

$$c = C \quad (7)$$

From eqn. (6) we in effect know the coefficients $|\alpha_i|$ to within the normalization

constant B. If we redefine the norm of the space spanned by the reaction coordinate, we can calculate the $|\alpha_i|$ and explicitly obtain our reaction coordinate from Eqn. (1).

There are several aspects of the above method that require examination. They are:

- (1) The question of the effects of overcompleteness and undercompleteness with respect to which internal coordinates are to be included in eqn. (1). Does undercompleteness imply failure of the method? Does inclusion of unnecessary coordinates cause undue algebraic labor?
- (2) The extent to which the quadratic assumption made in eqn. (3) is valid in regions of the space far removed from the vicinity of the transition state. Another functional form could also be assumed, i.e. a cubic form for E, and a method developed from it.
- (3) The use of various norms to solve eqn. (6). One might use a norm based upon $0 < \theta < 1$; a norm based upon the range of distances observed in the reactant state and product state or some other norm.

RESULTS

The method was first applied to the isomerization reaction of cis thionyl-imide, HNSO to cis thiazyl-S hydroxide, HOSN. This system was selected because this reaction has been studied in our laboratory and the potential energy surface is well understood by us, including the detailed structure of the transition state and the appropriate reaction coordinate.⁽⁸⁾ The structures of the reactant and product are shown in figure 1, that of the transition state is shown in figure 2. The reaction coordinate is a linear combination of the N-H, the N-S and the O-S bond distances. The internal angles do not play a major role.

The first point to be noted is that the method becomes very inefficient if the number of internal coordinates entering equation 1 becomes very large. In the table below are listed the number of data sets required (this is the same as the order of the set of linear algebraic equations to be solved) for a specific number of internal coordinates in the reaction coordinate.

Table

Number of Internal Coordinates Which Enter Reaction Coordinate	Number of Data Sets Required
1	2
2	5
3	9
4	14
5	20
6	27
7	35
8	44
9	54
15	135
21	252

It should be recalled that a fully optimized molecular orbital calculation must be performed to obtain a single data set.

The question of overcompleteness and undercompleteness with respect to

which internal coordinates must be included in equation 1 is critical. Omission of a critical coordinate will lead to a false maxima or an undesirable transition state. The inclusion of excess internal coordinates in equation 1 will cause unnecessary labor in the calculation.

The results obtained for the reaction coordinate seem to depend upon the choice of data sets. If the data sets consisted of a sampling of the potential energy surface near the transition state the method yielded the correct reaction coordinate. If the data sets selected spanned a wider area of the potential energy surface, the method generally did not converge directly to the reaction coordinate. This appears to be a severe limitation on the method. This may be due to the limitation of the use of a quadratic expression for the energy in terms of the reaction coordinate. It would be worthwhile to investigate other functional forms for equation 2.

Since the project only lasted for a brief period of eight weeks, the number of points that could be investigated was limited. The question of what the norm to use for the "normalization" of the reaction coordinate for example was only superficially examined. A norm based upon $|\alpha_i| \leq 1$ for all i was tried. It seemed to work well leading to

$$\phi = .0897583 d_{O-S} + 1.0 d_{S-N} + 0.186049 d_{H-N}$$

for the reaction coordinate.

In summary, the method is capable of yielding the correct reaction coordinate. It must be judicially applied requiring some considerable experience on the part of the user in the selection of the data sets to be employed. It possesses a real value in that it can be used to rapidly "zero in" on a transition state if the user has some a priori information as to the location of the transition state on the potential energy surface. It will be necessary to examine further test cases to ascertain its general applicability and

obtain an explicity answer as to whether it offers an efficient alternative to the present day trial and error procedure.

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Figure 1. Structures for the Cis Forms of Thionylimide
and Thiazyl-S-hydroxide

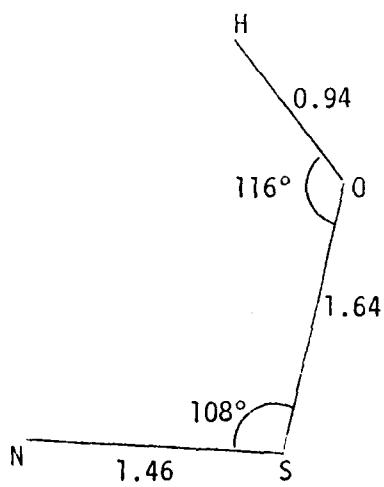
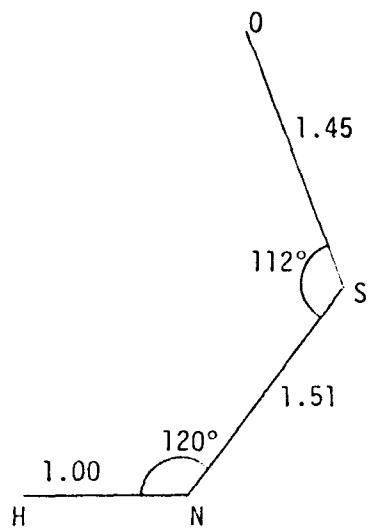
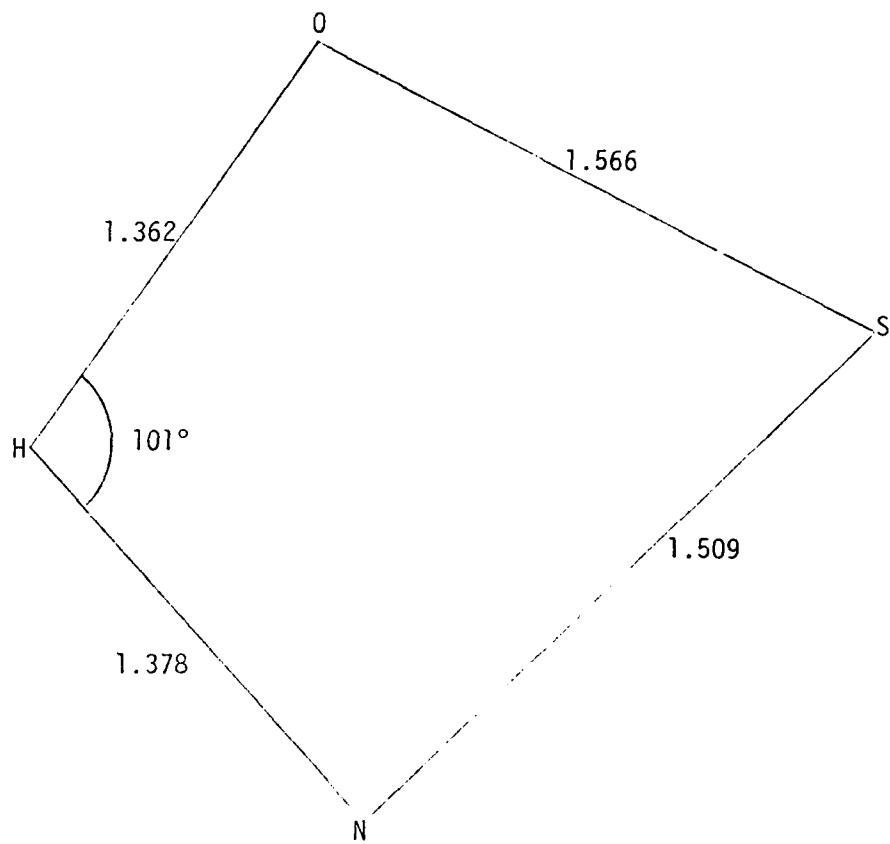


Figure 2. Structure of the Transition State.



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